

REVISION 2

THE NATURE OF Zn-PHYLLOSILICATES IN THE NONSULFIDE MINA GRANDE AND CRISTAL ZINC DEPOSITS (BONGARÁ DISTRICT, NORTHERN PERU): THE TEM-HRTEM AND AEM PERSPECTIVE

Giuseppina Balassone^{1,*}, Valentina Scognamiglio², Fernando Nieto³, Nicola Mondillo^{1,4}, Maria
Boni^{1,4}, Piergiulio Cappelletti¹, Giuseppe Arfè⁵

¹Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università degli Studi di
Napoli Federico II, Complesso Universitario Monte S. Angelo, Via Cintia 26, 80126 Napoli, Italy

²Via Tosi 4, Pozzuoli, Italy

³Departamento de Mineralogía y Petrología and IACT, Universidad de Granada, Granada, Spain

⁴Department of Earth Sciences, Natural History Museum, London, UK

⁵Via Staffetta 127, Giugliano, Italy

*Corresponding author: balasson@unina.it

RUNNING TITLE: Zn-phyllsilicates in the nonsulfide deposits of Bongará (Peru)

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ABSTRACT

27 Zn-phylosilicates are common minerals in nonsulfide Zn deposits and can give crucial information
28 on the genesis of these oxidized mineralizations. They seldom represent the prevailing economic
29 species but might have a significant impact on mineral processing. This study has been carried out
30 on the Mina Grande and Cristal Zn-sulfide/nonsulfide deposits, which occur in the Bongará district
31 (Amazonas region, northern Peru). The Cristal and Mina Grande orebodies are hosted by the
32 sedimentary (prevailing carbonate) successions of the Pucará Group (Condorsinga formation,
33 Lower Jurassic), in an area affected by Neogene tectonics and characterized by Late Miocene and
34 Pliocene-Early Pleistocene uplift phases (Andean and Quechua tectonic pulses). The Cristal deposit
35 consists of both sulfide (sphalerite with minor pyrite and galena) and nonsulfide concentrations.
36 The nonsulfides consists of smithsonite, hemimorphite, hydrozincite, chalcophanite, goethite and
37 greenockite, locally associated with Zn-bearing phyllosilicates. The Mina Grande deposit consists
38 almost exclusively of Zn-oxidized minerals in limestone host rocks. The nonsulfides association
39 consists of hydrozincite, hemimorphite, smithsonite, fraipontite and Fe-(hydr)oxides, also
40 containing a clayey fraction. The study deals with TEM-HRTEM and AEM investigations on
41 clayey materials, in order to determine their crystal-chemical features and the origin of the complex
42 Zn-clays-bearing parageneses. In both deposits, Zn-bearing illites ($1M_d$ and $2M$ polytypes) and I/S
43 clay minerals (I3) are the main detected phases, with few compositions close to (Zn-bearing)
44 muscovite. In the clayey fraction at Mina Grande, fraipontite, a Zn-bearing mica called K-deficient
45 hendricksite, and (Zn-bearing) kaolinite also occur. Zn-illites and smectites (always containing Zn
46 in variable amounts) characterize the mineral association at Cristal. The investigated compositional
47 gap between di- and tri-octahedral Zn-phylosilicates gives indications on the genetic relationships
48 between them and advances on the knowledge of these species. The present work gives an insight
49 into the Zn-bearing phyllosilicates systems, by determining the amount/mode of metal

50 incorporation in their lattices and understanding the relationships of natural occurring clay-rich
51 complex associations, which can act as models for possible synthetic counterparts.

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53 **Keywords:** Zn-phyllsilicates; Bongará; Cristal; Mina Grande; Peru; TEM-HRTEM; AEM

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INTRODUCTION

57 Zn-phyllsilicates are quite rare minerals, which can be found in most nonsulfide Zn deposits. In
58 this kind of ores, mainly derived from the weathering of primary sulfide concentrations, the Zn-
59 clays generally represent minor concentrations in the mineral assemblage, but they can also be the
60 prevailing economic minerals as in the world-famous Skorpion deposit in Namibia (Borg et al.
61 2003; Emselle et al. 2005; Kärner 2006; Boni and Mondillo 2015; Buatier et al. 2016; Choulet et al.
62 2016; Arfè et al. 2017; Balassone et al. 2017). Zn-clay minerals, formed in slightly acidic to neutral
63 conditions, are also commonly found in contaminated soils at mining and smelting sites (Manceau
64 et al. 2000; Juillot et al. 2003).

65 Sauconite (Ross 1946; Newman and Brown 1987), one of the most common clay minerals in
66 nonsulfide deposits (Large 2001; Hitzman et al. 2003; Boni, 2005, 2009a,b; Mondillo et al. 2014;
67 Boni and Mondillo 2015), is a trioctahedral saponite-like smectite with Zn in octahedral
68 coordination. Experimental studies on its synthesis and stability (i.e., Kloprogge et al. 1999;
69 Higashi et al. 2002; Petit et al. 2008; Pascua et al. 2010) demonstrated that sauconite can precipitate
70 from solutions of silicic acid, variously mixed with Zn-compounds (Zn-chlorides, Zn-oxides, or Zn-
71 hydroxides) and Na- and Al compounds, at a pH interval of 6–12 and temperatures ranging between
72 20 and 200 °C. Among the other Zn-phyllsilicates, the mineral fraipontite, belonging to the
73 kaolinite-serpentine group and the serpentine subgroup (Fransolet and Bourguignon 1975), and
74 baileychlore, a member of the chlorite group (Rule and Radke 1988), also occur in some nonsulfide

75 ore deposits. Recently, Mondillo et al. (2015) and Balassone et al. (2017) studied the Zn-
76 phyllosilicates from Accha and Yanque (Peru) and Skorpion (Namibia), respectively, by means of
77 transmission electron microscopy - high resolution TEM (TEM-HRTEM) analyses. Kaufhold et al.
78 (2015) characterized the Zn-bearing smectites from the Silver Coin Mine (USA). Buatier et al.
79 (2016) and Choulet et al. (2016) described Zn-clays consisting of interstratified fraipontite/smectite
80 (fraipontite-prevailing), closely associated to willemite ores in several nonsulfide Zn deposits from
81 the Moroccan High Atlas, formed by direct precipitation of meteoric and/or hydrothermal fluids.
82 Generally speaking, Zn-clays are not only an ore resource but also a drawback, because they can
83 negatively affect the industrial treatment to a various extent (Choulet et al. 2016, and references
84 therein). Hence, their detailed mineralogical study is particularly useful from the perspective of
85 industrial and economic evaluations.

86 Zn-phyllosilicates had been already detected in the Mina Grande and Cristal sulfide and nonsulfide
87 deposits, located in the Bongará area in northern Peru (Arfè et al. 2017a,b, 2018; Arfè 2018;
88 Mondillo et al. 2018a,b). In these mineralizations, sulfide minerals are mostly represented by
89 sphalerite and by minor galena and pyrite, weathered to a nonsulfide assemblage mostly consisting
90 of smithsonite, hemimorphite, and hydrozincite. Arfè et al. (2017b, 2018) and Arfè (2018) detected
91 variable amounts of different Zn- phyllosilicates in the complex mineral assemblages of the
92 Bongará mining district. A first detailed mineralogical identification of the Zn-rich clayely
93 assemblages of the Mina Grande and Cristal supergene deposits was carried out by Arfè et al.
94 (2017a) by combined scanning electron microscopy with energy dispersive X-ray spectroscopy
95 (SEM-EDS) and X-ray powder diffraction (XRPD). According to the latter work, the main sheet
96 silicates occurring in both deposits were considered I/S (illite/smectite) mixed layers, partly altered
97 or overprinted by sauconite. Fraipontite (the Zn-member of the kaolinite-serpentine group) has been
98 found only at Mina Grande, locally associated with minor zaccagnaite (a rare hydrated Zn-Al
99 carbonate, member of the hydrotalcite supergroup and quintinite group; Merlino et al. 2001; Lozano

100 et al. 2012; Mills et al. 2012), whereas a Zn(Mn) mica similar to hendricksite (a Zn-Mn
101 trioctahedral potassic mica; Robert et al. 1985) was detected at Cristal.

102 However, due to the micro- to nano-sized nature of the Bongará phyllosilicates, as well as to the
103 presence of diffuse impurities, typically consisting of Fe(Mn)-(hydr)oxides (i.e. goethite,
104 chalcophanite, etc.), some questions still remained open, thus requiring a specific study of the clay
105 fraction. The issues in need of a better clarification concerned: (i) a more accurate characterization
106 of the widespread Zn-layered silicate varieties generically identified as Zn- micas (or illites), as well
107 as of the I/S interstratified clay minerals, (ii) the ascertainment of hendricksite-type mica, (iii) the
108 definition of the smectite(s) types and of other possible clays (or also other possible Zn- minerals),
109 (iv) if the occurrence of fraipontite should be confined only to Mina Grande deposit.

110 In order to answer these questions and determine the true nature of the Zn- phyllosilicates, we have
111 carried out detailed TEM and scanning TEM (STEM) and HRTEM investigations down to the
112 nanoscale on the clay-rich fraction of a few selected samples already studied by Arfè et al. (2017a).
113 This approach has allowed to analyze the purest mineralogical phases and has consequently helped
114 resolving the issues above exposed. The present research was also aimed at identifying the
115 processes accounting for the genesis of the Zn-phyllosilicates, with implications to their potential
116 for zinc recovery.

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119 **GEOLOGY AND MINERALIZATION OF THE BONGARÁ AREA**

120 Bongará is a province of the Amazonas Region in Peru, located approximately 740 km north of
121 Lima and 245 km northeast of the coastal city of Chiclayo. It is situated on the western margin of
122 the Subandean foreland basin of northern Peru, within the mountainous terrain of the Subandean
123 fold-and-thrust belt (Fig. 1a) (Arfè et al. 2018). The geology of the northern Andes, where Bongará
124 is located, underwent two important orogenic cycles (Benavides-Caceres 1999), i.e. the pre-Andean

125 (Precambrian to Paleozoic) and Andean (Early Jurassic to Present) cycles. The sedimentary Pucará
126 Basin developed in correspondence of the current Eastern Cordillera, within a NW-trending sinistral
127 shear zone (Mégard 1987; Benavides-Caceres 1999; Rosas et al. 2007). The basin started to be
128 filled with up to 3000 m thick continental siliciclastics of the Mitu Group (Middle to Late Triassic)
129 (Arfè et al. 2017a, 2018), which include red sandstones, mudstone, polymictic conglomerates and
130 rare pyroclastic rocks (Fig. 1b). At the same time, it underwent a fault-controlled subsidence, which
131 was gradually followed by a regional subsidence associated with NW to NNW-trending sinistral
132 shear zone from Late Triassic to Early Jurassic (Mégard 1984; Benavides-Caceres 1999; Rosas et
133 al. 2007). From Late Triassic to Early Jurassic, the sediments of the Pucará Group filled the basin
134 with shallow- to deep-water marine carbonates, unconformably deposited over the sediments of the
135 Mitu Group (Fontboté 1990; Reid 2001; Rosas et al. 2007). The Pucará Group Units are
136 stratigraphically subdivided in basal Chambará Formation consisting of thinly bedded limestone
137 and silty shale, overlying bituminous calcareous Aramachay Formation and uppermost Condorsinga
138 Formation with its bioclastic and cherty limestone (Brophy et al., 2012). During Toarcian, a
139 regional uplift promoted erosion and karstification of the top of the Condorsinga carbonates
140 (Mondillo et al. 2018a), leading to the formation of cavities and depressions. As a consequence, the
141 continental sequences of the Sarayaquillo Formation (Upper Jurassic to Cretaceous), which consist
142 of red shales, sandstones and marls (Arfè et al. 2017b; Arfè 2018), were deposited in various
143 colluvial, alluvial and lacustrine environments together with gypsum beds (Rosas et al. 2007) in
144 angular unconformity above the Condorsinga Formation (Fontboté 1990; INGEMMET 1995). The
145 lower Cretaceous in the Bongará area is characterized first by a major marine transgression, which
146 led to the deposition of siliciclastic rocks of the Goyllarisquizga Group, and then of argillaceous
147 limestones with nodular silty mudstones (Mondillo et al. 2018a) of the Chonta-Chulec Formation.
148 The area of interest for this study has been affected by Neogene tectonics from 20.5 to 1.6 Ma,

149 characterized by Late Miocene and Pliocene-Early Pleistocene uplift phases, among which the
150 Andean and Quechua tectonic pulses (Arfè et al. 2017a,b, 2018; Arfè 2018; Mondillo et al. 2018a).
151 The Pucará Basin includes many types of ores in central and northern Peru (Kobe 1977, 1982,
152 1990a,b; Dalheimer 1990; Fontboté 1990; Reid 2001), mainly corresponding to Mississippi Valley-
153 type (MVT) Zn-Pb deposits. The most intensive exploration in the Bongará area was carried out in
154 the Charlotte Bongará permit (which includes the Mina Grande and Cristal occurrences) in the
155 north, and in the Florida Canyon permit, in the south. These deposits consist of stratabound Zn-Pb
156 nonsulfide/sulfide concentrations (Wright 2010; Boni and Mondillo 2015). The formation of
157 supergene nonsulfide mineralization is closely related to the tectonics of the area, which led to
158 uplift, uncapping, weathering and alteration of several exhumed sulfide orebodies (Arfè et al.
159 2017b).

160 Mina Grande and Cristal are hosted by Mesozoic limestones and dolostones of the Condorsinga
161 Formation. The Mina Grande deposit consists totally of nonsulfides, derived from the weathering of
162 MVT ores. The mineralization contains supergene zinc minerals such as smithsonite, hemimorphite,
163 hydrozincite but also of Zn-phyllsilicates. Mina Grande was partly mined in open-pit in three
164 different areas (A, B and C Phases) and is currently under exploration. The Cristal deposit is a
165 mixed sulfide and nonsulfide mineralization, with the latter resulting from alteration and dissolution
166 of the sulfide protore. The presence of sulfides still in place at Cristal (Mondillo et al. 2018a)
167 combined with the absence of any obvious recent karstic activity, suggests that supergene alteration
168 acted in two different ways in the two respective localities (Arfè et al. 2018).

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MATERIALS AND METHODS

172 The transmission electron and analytical electron microscopy (TEM-AEM) study was conducted on
173 four samples (ZB-1, ZB-2, CR07-13, CR13-7) collected from the Mina Grande and Cristal

174 nonsulfide deposits (Fig. 2), during a field survey carried out in 2016. These (sub)samples come
175 from drill cores and hand-specimens already mentioned in Arfè et al. (2017a). In order to select the
176 richest clayey fractions of the samples for successive TEM-AEM investigations, preliminary
177 mineralogical analyses were carried by combined X-ray powder diffraction (XRPD) and SEM-EDS
178 at the Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse (DiSTAR) University of
179 Naples Federico II, Italy (XRD equipment: Seifert-GE ID3003 diffractometer, with CuK_α radiation,
180 Ni-filtered at 40 kV and 30 mA, 3–80 $^\circ 2\theta$ range, step scan 0.02 $^\circ$, time 10 s/step, and RayfleX (GE)
181 software package; SEM-EDS equipment: JEOL JSM5310 electron microscope with Oxford EDS,
182 INCA X-stream pulse processor with 4.08 Inca software, operating conditions at of 15 kV and 20
183 mm working distance).

184 Textural observation of clays at the micro- and nanoscale and chemical analyses were performed on
185 thin sections by combining TEM with high resolution transmission electron microscopy (HRTEM),
186 scanning transmission electron microscopy (STEM) and high-angle annular dark field (HAADF)
187 investigations, carried out at the Centro de Instrumentación Científica (CIC) of the University of
188 Granada (Spain). Copper rings were attached to representative selected areas of the matrix of thin
189 sections prepared with Canada balsam and after ion-thinned, using a Fischione Model 1050 ion
190 mill, and carbon coated. Ion milling was performed at 4 kV and $\pm 10^\circ$, until the first hole and $\pm 7^\circ$
191 during 20 min for final cleaning. We used a Titan TEM with XFEG emission gun, spherical
192 aberration image corrector and HAADF detector, working at 300 kV, with a resolution of 0.8 Å in
193 the TEM mode and 2 Å in the STEM mode. Qualitative vs. quantitative chemical identification of
194 minerals and chemical maps were obtained by AEM-EDX (energy dispersive X-ray spectroscopy)
195 analyses using the Super-X system. Quantitative analyses, presented in Tables 2-5, were obtained
196 using albite, biotite, muscovite, spessartine, olivine, titanite, and hemimorphite as standards,
197 measured using the same protocol as samples (Abad and Nieto 2003), to obtain K-factors for the
198 transformation of intensity ratios to concentration ratios, according to Cliff and Lorimer (1975). In

199 order to avoid contamination problems (mainly due to widespread goethite and other oxy-
200 hydroxides), several chemical analyses were rejected, and only those as pure as possible have been
201 accepted. Electron diffraction patterns (selected area electron diffraction, SAED) were carried out,
202 whenever possible, in the same areas investigated by TEM-AEM. Additional investigations on
203 particle morphology and quantitative chemical analyses were obtained by using a TEM Philips
204 CM20 (CIC, Granada), operating at 200 kV, with an EDAX solid-state EDX detector. Lifetime of
205 the analyses was 100 s; areas producing dead time higher than 5% were rejected to ensure the thin
206 character required by the Cliff and Lorimer (1975) approximation. Analyses were obtained using
207 STEM mode, from powdered portions deposited on a holey C-coated Au grid. This mode of
208 preparation disperses individual grains of minerals onto the grid surface. Albite, biotite, muscovite,
209 spessartine, olivine, titanite, and hemimorphite standards were measured using the same protocol as
210 the samples.

211 Ideal chemical formulae of the main minerals quoted in this work are listed in Table 1.

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RESULTS

215 The TEM-AEM study has pointed out that the main phyllosilicate detected in the clay-rich fractions
216 of the supergene assemblage of Bongará is being identified as illite, which always contains Zn
217 (\pm Fe,Mn) in variable amounts (Tables 2-5), hence corresponding to a Zn-bearing illite. These
218 chemical variations describe a particular outline and represent, in our opinion, a key point for the
219 definition of this kind of Zn-sheet silicates, as it will be discussed more in detail in the following
220 paragraphs. Taking into account that AEM allows determining the ratios between the various
221 elements, it is required to normalize the obtained chemical compositions to the basic formula of the
222 investigated minerals. Hence, on the basis of the composition of Zn-bearing illites, we have mainly
223 distinguished two varieties:

224 - Zn(Fe)-poor and Al^{VI}-rich varieties, in brief indicated hereafter as Zn-illites, and considered as
225 dioctahedral. Their structural formulas have been calculated on the basis of 6 (IV+VI) cations, as
226 suggested by Nieto et al. (2010) for dioctahedral species of illite;

227 - Zn(Fe)-rich and Al^{VI}-poor varieties, which we have considered as a mixture of
228 dioctahedral/trioctahedral species and abbreviated to MDT Zn-illites hereafter (see also
229 Discussion). For these mixed compositions, the structural formulas have been recalculated on the
230 basis of 11 oxygens.

231 Other significant Zn-bearing mineral/associations have been detected in minor to trace amounts in
232 the two sampled occurrences (Mina Grande and Cristal), and are described in the following
233 paragraphs.

234

235 **Mina Grande**

236 Tables 2 and 3 show representative AEM analyses of Zn-illite and MDT Zn-illite in the Mina
237 Grande samples (ZB-1 and ZB-2), with the second variety definitely prevailing over the first one.

238 Zn-illite shows the tetrahedral cations in the range 3.06-3.14 apfu for Si (average, av. hereafter,
239 equal to 3.10 apfu) and 0.86-0.94 apfu for Al^{IV} (av. 0.90 apfu); regarding the octahedral cations, Zn
240 is in the interval 0.31-0.40 apfu (av. 0.36 apfu), Mg 0.19-0.26 apfu (av. 0.23 apfu), Fe 0-0.01 apfu
241 (av. 0.01), Ti 0-0.03 apfu (av. 0.02 apfu), whereas Al^{VI} is in the range 1.31-1.49 apfu (av. 1.40
242 apfu). The interlayer cation K varies in the range 0.70-0.75 apfu (av. 0.73 apfu). Fig. 3a shows a
243 common texture of Zn-illite, often associated with fraipontite mainly occurring as cavity fillings.
244 The SAED-HRTEM investigations (Fig. 3b) demonstrate that illite is characterized by lattice
245 fringes and 00l spots in the SAED with *d*-spacings always around 10 Å. The rest of the rows (non-
246 00l) in the SAED, which could allow the identification of the mica polytypes, are represented by
247 continuous lines, indicating a disordered polytype 1M_d. The lattice fringe images of Fig. 3c show
248 misorientation among the packets, typical of illite. The various packets have different

249 crystallographic orientation, at less [100] and [110] zone axis have been identified from partial
250 periodicity which can be recognized along some layers and allows identification of very local order,
251 corresponding to 1*M* polytype of illite. In the FFT of the image 3c (inset), together with those
252 orientations, also [010] can be identified. The misorientation among the various packets is
253 responsible of the disordered character of the polytype identified for the whole area in the SAED.
254 However, in the same image the textures can be interpreted as belonging to illite/smectite mixed
255 layers (I/S) of I3 type, due to the minor presence of smectite layers, characterized by different
256 contrast and spacing (12 Å), separated by at less 3 illite layers¹. Smectite layers collapse variably
257 between 17 and 10 Å, being the latter their most frequent value, in the vacuum of the microscope,
258 principally depending on their local interlayer composition (Nieto et al, 1996). Periodicity of 52 Å
259 (4 illite layers + 1 smectite layer) can be also identified in the FFT. Fig. 3e shows a chemical map
260 of a Zn-illite (+fraisontite, Fe,Ti-oxy-hydroxides) area and its typical EDX spectrum, with the small
261 but always present peak of Zn.
262 Compositions referred as to MDT Zn-illite (Tables 2 and 3) show the tetrahedral cations in the
263 range 2.57-3.17 apfu for Si (av. 2.90 apfu) and 0.83-1.43 apfu for Al^{IV} (av. 1.10 apfu); in the
264 octahedral site, Zn is in the interval 0.29-1.44 apfu (av. 0.77 apfu), Mg 0.15-0.46 apfu (av. 0.26
265 apfu), Fe up to 0.81 apfu (av. 0.37 apfu), Ti up to 0.52 apfu (av. 0.20 apfu) and Al^{VI} is in the range
266 0.43-1.42 apfu (av. 0.92 apfu), whereas K is in the interval 0.48-0.90 apfu (av. 0.62 apfu). Fig. 4a
267 shows a textural image of an area of sample ZB-1 particularly rich in MDT Zn-illite; its electron
268 diffraction pattern is shown in the bottom-right inset of Fig. 4a, and represents rows with spacings
269 of 10 Å. Figs. 4b,c,d,e also shows the association of MDT Zn-illite with fraipontite and Fe,Ti,Mn-

¹ The notation I3 refers to the nomenclature for interstratifications as reported by Vázquez et al. (2016) and Bauluz et al. (2000). Indeed, according to these authors, ordering in interstratified I/S, ordinarily characterized by its *Reichweite* value (*R*) based on X-ray diffraction data, representing long-range ordering averaged over all the layers that scatter X-radiation; TEM images can identify short-range ordering of interlayers within I/S packets, and the *Reichweite* nomenclature results inappropriate for specific layer sequences as observed by TEM. Hence the notation *I_n*, analogous to the *Reichweite* nomenclature, can be employed but applied only to specific layers, where *n* is the number of illite-like layers associated with a given smectite-like (see Vázquez et al. 2016, and references therein, for further details).

270 oxy-hydroxides. The 1:1 phyllosilicate is often in individual recognizable crystals significantly
271 bigger than those of micas, reaching a maximum length of 3 μm .

272 Fig. 5 shows a remarkable feature involving these Zn-layered silicates and observed in an area of
273 approximately 1 μm^2 . Figs. 5a and 5b, respectively, illustrate a textural image and the related
274 chemical map of sample ZB-2, where illites show variable amounts of Zn in the packets; here they
275 occur with fraipontite and subordinate kaolinite and Fe-Ti-oxides. If the AEM map of Fig. 5b is
276 compared with the chemical mappings of selected elements of Fig. 5c, the illite-rich area is
277 significantly well-defined by the K map and displays a complex textural organization. Indeed, in
278 this zone, while K is homogeneously distributed, Zn is highly heterogeneous, resulting in fine
279 intergrowths between MDT Zn-illite, with 1.28 apfu of Zn (see analysis. # 3.cuan-MAP1 of Table
280 3, and EDX spectrum 2 of Fig. 5d), and Zn-illite, with 0.31 apfu of zinc (see analysis # 6.cuan,
281 Table 3, and EDX spectrum 1 of Fig. 5d). The inference of this particular compositional and
282 textural organization, relevant to the origin of Zn-phyllosilicates, will be discussed more in detail in
283 the section "Discussion". High resolution TEM investigation of this zinc illite (inset in Fig. 5)
284 illustrates stacking of 10 Å periodicity, which is in agreement with this type of sheet silicate.

285 Another second distinctive finding in the Mina Grande samples is a well-defined Zn-mica
286 (illustrated in Tables 2, 3 and Fig. 6), having an octahedral population with Zn in the range 1.55-
287 1.89 apfu (av. 1.66 apfu), Fe 0.13-0.20 apfu (av. 0.15 apfu) and Mg up to 0.14 apfu (av. 0.15 apfu),
288 (Tables 2 and 3); Si is the range 2.87-2.92 apfu (av. 2.89 apfu) and Al^{IV} 1.08-1.13 apfu (av. 1.11
289 apfu), whereas K shows an interval of 0.57-0.70 apfu (av. 0.64 apfu) (Tables 2 and 3). In
290 accordance with the guidelines reported in the classification of micas (Rieder et al. 1998),
291 hendricksite is characterized by $\text{Zn} > 1.5$ apfu and $\text{K} < 1$. Hence the Zn-mica detected here can be
292 defined as hendricksite, even if this mica typically shows an "illitic" character (lower K amounts,
293 presence of Al^{VI}). For this reason, we named it K-deficient hendricksite. Fig. 6 shows Zn-
294 phyllosilicates dispersed particles in sample ZB-2, composed of K-deficient hendricksite, Zn-illite

295 and fraipontite, with the qualitative chemical spectra of selected areas of the zinc mica and
296 serpentine.

297 Fraipontite was detected in the Mina Grande samples. Fig. 3d shows stacking of 7 Å periodicity,
298 typical of this Zn phyllosilicate. Fig. 4c illustrates an association of fraipontite and MDT Zn-illite at
299 the nanoscale; the electron diffraction pattern in the inset suggests an epitaxial or topotaxial
300 relationship between the two minerals, as they share the c^* parameter. Due to the paragenetic
301 relations between these 2:1 and 1:1 phyllosilicates, it is reasonable to assume that fraipontite grew
302 onto illite. Chemical compositions of fraipontite (Tables 2 and 3) show tetrahedral cations within a
303 range of 1.08-1.40 apfu for Si (av. 1.23 apfu) and 0.60-0.92 apfu for Al^{IV} (av. 0.76 apfu); the
304 octahedral cations range from 2.19 to 2.96 apfu for Zn (av. 2.54 apfu), from 0.34-0.68 apfu for Al^{VI}
305 (av. 0.50 apfu) and from 0.04 to 0.14 apfu for Fe (av. 0.10 apfu).

306 Kaolinite was detected in very subordinate amounts only in sample ZB-2 (Table 3). In the
307 tetrahedral site Si is in the range of 2.00-2.10 apfu (av. 2.05 apfu), whereas the octahedral
308 population is composed of 1.44-1.66 apfu Al^{VI} (av. 1.54 apfu), as well as of small amounts of Mg
309 (0.13 apfu) and Zn (0.12-0.70 apfu, av. 0.14 apfu).

310 Finally, Fig. 7a and 7b respectively show HAADF and chemical mapping of an area of sample ZB-
311 2 where tiny cavity-lining and tapering crystals of supposed zaccagnaite can be observed together
312 with Zn-illite, fraipontite and oxides (Table 1). These crystals are Zn-rich and appear
313 morphologically slightly different from fraipontite crystals; the EDX spectrum displays high Zn, C
314 and O peaks, compatible with a zinc carbonate, whereas the chemical map of Si indicates the virtual
315 absence of this element in the areas of possible zaccagnaite occurrence. Even though
316 smithsonite/hydrozincite could also be a reasonable option, the occurrence of zaccagnaite in the
317 Mina Grande samples has been already proved by Arfè et al. (2017a). Because of the nano-sized
318 dimension of these crystals and the close association with fraipontite, it was impossible to obtain
319 chemical analyses and SAED-HRTEM images for validating this phase.

320

321 **Cristal**

322 Similarly to Mina Grande, also in the Cristal samples CR07-13 and CR13-7 (Fig. 2) illites, both Zn-
323 and MDT Zn-illites, are always the prevailing minerals detected in the supergene assemblage. Here
324 the varieties referred as Zn-illite prevail over the MDT types (Tables 4 and 5), if compared with
325 Mina Grande. Furthermore, differently from Mina Grande, and in agreement with Arfè (2018), K-
326 deficient hendricksite and fraipontite have been not detected, at least in the investigated samples.

327 In the Cristal Zn-illites (Tables 4 and 5), the tetrahedral cations are in the range 3.18-3.66 apfu for
328 Si (av. 3.36 apfu) and 0.42-0.82 apfu for Al^{IV} (av. 0.64 apfu); in the octahedral site, Zn is in the
329 interval of 0.04-0.27 apfu (av. 0.10 apfu), Mg 0.16-0.32 apfu (av. 0.29 apfu), Fe up to 0.21 apfu (av.
330 0.11), whereas Al^{VI} is in the range 1.41-1.11 apfu (av. 1.50 apfu). Regarding the interlayer cation K,
331 it varies in a range of 0.34-0.72 apfu (av. 0.61 apfu). As illustrated in Tables and 5, few values of K
332 indicate compositions close to a (Zn-bearing) muscovite, rather than illite. In particular, if we
333 consider three analyses of sample CR07-13 (Table 4, # anl. 5, anl. 11 and 1.cuan-MAP2) and two
334 analyses of sample CR13-7 (Table 5, # 3.cuan-MAP4 and 11.cuan-MAP5) in relation to the ideal
335 muscovite formula established by Rieder et al. (1998), these compositions fulfill the condition of
336 the interlayer cation (K) amounts in the range 0.7-1.0 apfu (or $I \geq 0.85$ apfu), as well as the
337 condition of Si = 3.0-3.1 apfu in the majority of cases; however, the ^{VI}Al values of these analyses
338 do not fully satisfy the standard muscovite ranges reported by Rieder et al. (1998) (1.9-2.0 apfu),
339 and also most of the calculated $\text{VI}R^{2+}/(\text{VI}R^{2+} + \text{VI}R^{3+})$ ratios are slightly higher (0.30 apfu on average)
340 than the muscovite range (i.e. <0.25 apfu). These Zn-bearing muscovites show the following
341 ranges: Si 2.89-3.39 apfu (av. 3.19 apfu) and Al^{IV} 0.61-1.811 apfu (av. 0.81 apfu), with Al^{VI} 0.90-
342 1.66 (av. 1.50 apfu), Zn 0.07-0.15 apfu (av. 0.11 apfu), Mg 0-0.29 apfu (av. 0.18 apfu), Fe up to
343 0.84 apfu (av. 0.29) and Mn 0-0.65 apfu (av. 0.12 apfu) in the octahedral site. The interlayer cation
344 K is in the range 0.81-1.07 apfu (av. 0.95 apfu).

345 Fig. 8 shows the chemical mapping of Zn-illite, which can contain differently Zn-enriched packets
346 varying from Zn of 0.04 apfu (see analysis # 3.cuan-MAP1 of Table 4 and EDX spectrum 1 of Fig.
347 8c) to Zn equal to 0.21 apfu (see analysis # 1.cuan-MAP1 of Table 4 and EDX spectrum 2 of Fig.
348 8c). The SAED-HRTEM investigation is reported in Fig. 8b, where rows with stacking of 10 Å
349 periodicity can be observed.

350 Subordinate MDT Zn-illite (Tables 4 and 5) shows the tetrahedral cations in the range 2.67-2.93
351 apfu for Si (av. 2.78 apfu) and 1.07-1.33 apfu for Al^{IV} (av. 1.22 apfu); the octahedral cations vary
352 from 0.51-0.60 apfu for Al^{VI} (av. 0.54 apfu), 0.39-0.86 apfu for Zn (av. 0.65 apfu), 0.28-0.98 apfu
353 for Mn (av. 0.72 apfu), 0.60-1.07 apfu for Fe (av. 0.86 apfu) and up to 0.26 apfu for Mg (av. 0.09
354 apfu). Compared with the same varieties detected at Mina Grande, these illites are Mn-bearing and
355 Ti-free. Due to the rarity of MDT type, it was not possible to find suitable crystalline particles for
356 recording their lattice fringes images and/or electron diffraction patterns of acceptable quality.

357 Fig. 9a and 9b show typical textural images of the Zn-illite at Cristal. The top right inset of Fig. 9a
358 shows the electron diffraction pattern with differences of orientation among the various packets;
359 rows with periodicity of 14 Å can be due to smectite. In the right inset of Fig. 9b, the less visible
360 row corresponds to [100] (20 Å, 2M polytype), and the more visible to [010]. Diffraction points
361 corresponding to (h0l) have systematic extinctions for *l* odd, therefore they do not allow the
362 polytype identification. The left inset of Fig. 9b also illustrates the SAED pattern of a disordered
363 polytype (1M_d). Fig. 9c and 9d respectively illustrate lattice image of packets with I/S mixed layers
364 having minor proportion of smectite layers (I3) and slightly disoriented packets, typical of illite.

365 Fig. 10 illustrates another characteristic of the zinc phyllosilicates at Cristal; here smectite occur
366 both as nanoscale interleaved (Fig. 10a) phase with Zn-illite and in larger particles (Fig. 10b); high
367 resolution TEM images show that the small packets are internally ordered with stacking of 10 Å
368 (Zn-illite) and 13 Å (slightly collapsed smectite) periodicities. Smectites detected in the Cristal
369 samples correspond to beidellite, which always contain small amounts of Zn (0.02 apfu) and

370 sauconite (see the EDX spectra of Fig. 10 and Table 5). As shown in Fig. 10b, sauconite seems also
371 to replace zinc illite. Finally, a composition attributable to montmorillonite, with small but
372 detectable Zn amount (0.14 apfu) was also locally found (Fig. 10a and Table 5).

373

374 **Overall crystal-chemical features of the Bongará phyllosilicates**

375 Bivariate diagrams of selected elements of the detected phyllosilicates are reported in Fig. 11. In the
376 Al_{tot} vs. Si diagram (Fig. 11a), zinc illites are generally enriched in these elements compared with
377 MDT Zn-illites, even though some Si-depleted compositions fall in the field of the latter illites. K-
378 deficient hendricksite entirely plots in the area of MDT Zn-illite, being indistinguishable from these
379 illites in terms of Si and Al_{tot} contents. Fraipontites cluster in a well-constrained field, as well as
380 kaolinites. Sauconite compositions are characterized by variable Si and Al amounts, as already
381 observed by Mondillo et al. (2015) and to a lesser extent by Balassone et al. (2017), and possibly
382 attributable, at least in part, to interstratifications with illite layers.

383 The Zn vs. Al^{VI} plot (Fig. 11b) shows a positive correlation of EDX data, illustrating a distinction
384 between dioctahedral and trioctahedral species; MDT Zn-illite compositions fall in a quite wide
385 area, placed between the Zn-illite and the K-deficient hendricksite fields. MDT Zn-illite is variable
386 in term of both Zn and Al^{VI} , whereas Zn-illites show an evident chemical variability mainly in term
387 of Al^{VI} content. Hendricksite is better constrained if compared with the diagram of Fig. 11a (even
388 though only three compositions were measured at Mina Grande). Obviously, fraipontite/sauconite
389 and kaolinite/beidellite/montmorillonite occupy the opposite sides of trioctahedral and dioctahedral
390 compositional fields, respectively.

391 Fig. 11c illustrates the Zn vs. K diagram, which shows a similar trend as the previous plot; the
392 dioctahedral and trioctahedral compositions fall in well-defined fields, with MDT Zn-illite
393 compositions scattered between the Zn-illite and the K-deficient hendricksite fields. The major
394 chemical variability of Zn-illite is related to the K cation, differently from MDT Zn-illite

395 compositions, which are more variable in terms of both Zn and K contents. Indeed, while in
396 bivariate plots of Fig. 11a and 11b compositions approaching muscovite cannot be distinguished
397 from the other Zn-illites, in the diagram of Fig. 11c mica-related compositions are obviously better
398 constrained, due to their higher K amounts. Dioctahedral smectites plot in the Zn, K-poor side.
399 In the $M^{+}-4Si-3R^{2+}$ ternary diagram (Fig. 12a), used for discriminating the dioctahedral and the
400 trioctahedral compositions (Meunier 2005), our Zn-illites are scattered along the mixing line of
401 muscovite-sauconite-fraipontite ideal compositions and rather plot into an intermediate domain
402 between the muscovite and sauconite poles. As illustrated in Tables 4 and 5, some compositions
403 more correctly plot close to muscovite end-member, whereas other Zn-illites, as well as MDT Zn-
404 illites are more scattered, indicating that clays are generally mixed compositions. In this plot, K-
405 deficient hendricksite also plots along the muscovite-sauconite join and into the MDT Zn-illite
406 field, in slightly different position if compared with the ideal hendricksite. Fraipontite plots very
407 close to the theoretical compound, whereas other clay minerals, i.e. smectites and kaolinite, are
408 more scattered due to their chemical variability (i.e. Zn in kaolinite).
409 In the K-Zn-Al^{VI} ternary diagram of Fig. 12b all Zn-illites plot into an intermediate area between
410 ideal muscovite and K-deficient hendricksite; Zn-illite, MDT Zn-illites and K-deficient hendricksite
411 occupy three different domains, fairly well-defined but continuous, indicating that zinc clays are
412 dominantly a mixture of two end-members *sensu lato* approaching theoretical muscovite and
413 hendricksite, that we have considered to be respectively Zn-illite and K-deficient hendricksite (see
414 the next paragraph). As might be expected, compositions close to (Zn)muscovite plot in a better
415 defined, K-rich, area. Fraipontite again plots in a restricted field, confirming its homogenous
416 composition, as well as smectites (both dioctahedral and trioctahedral), even if based on few point-
417 analyses.

418

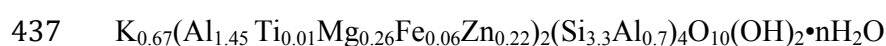
419

DISCUSSION

420 **Mineral identification**

421 Guggenheim et al. (2006) listed illite as a dioctahedral species in the interlayer-deficient mica
422 group. However, following the proposal by Rieder et al. (1998), Guggenheim et al. (2007)
423 subsequently considered illite to be only a series name. Besides showing a variety of chemical
424 compositions, many illite samples are essentially mixed-layer structures, with smectite usually
425 making up the other component although the presence of interstratified smectite layers is difficult to
426 detect when their proportion is less than 10%. The chemical composition of illite has been
427 extensively studied by many authors (i.e. Środon and Eberl 1984; Brigatti and Guggenheim 2002;
428 Meunier and Velde 2004; Meunier 2005; Nieto et al. 2010; Escamilla-Roa et al., 2016), and
429 according to the International Mineralogical Association (IMA) nomenclature committee the term
430 illite should be used to designate interlayer-cation-deficient (<0.85 apfu) micas (Rieder et al. 1998).
431 Then, following the nomenclature suggested by Rieder et al. (1998), illite has a general formula
432 $K_{0.65}Al_{2.0}\square Al_{0.65}Si_{3.35}O_{10}(OH)_2$, with $^{VI}R^{2+}/(^{VI}R^{2+} + ^{VI}R^{3+}) \leq 0.25$, and can refer to a relatively
433 large volume in compositional space, as a counterpart to glauconite. To summarize, we established
434 that the Zn-illite investigated in the present study, and often reported by Arfè et al. (2017a,b) simply
435 as Zn-mica, is very similar to illite *sensu* Reider et al. (1998); its mean formula can be expressed as:

436



438

439 The occurrence of Mg and Fe is a common characteristic for illite, but, if we compare the
440 theoretical formula of illite with this case of study, the remarkable aspect is that its packets also
441 show variable Zn concentration (e.g. Fig. 8). In the ordered illite polytype (mainly observed at
442 Cristal), the apparent disorder is only due to the small dimension of the packets with different
443 orientation and does not reside in the packet itself, as normally observed in illite. At Mina Grande,
444 instead, a true disordered polytype ($1M_d$) has been found. Besides, the minor occurrence of smectite

445 layers, attributable to R3 type I/S mixed layers, has also been observed in the investigated samples
446 (Figs. 3 and 9). Compositions ascribed to Zn-bearing muscovite, found in the Cristal samples only,
447 can be expressed by the average formula $K_{0.95}(Al_{1.30}Mg_{0.18}Fe_{0.29}Mn_{0.12}Zn_{0.11})_2$
448 $(Si_{3.19}Al_{0.81})_4O_{10}(OH)_2 \cdot nH_2O$.

449 Many mixed compositions between Zn-illite and K-deficient hendricksite, i.e. MDT Zn-illites, are
450 recognized in this study. K-deficient hendricksite has the following average empirical formula:

451

452 $K_{0.64}(Al_{0.86}Mg_{0.15}Fe_{0.15}Zn_{1.66})_{2.82}(Si_{2.89}Al_{1.11})_4O_{10}(OH)_2$.

453

454 From the TEM study, this mica appears to be Mn-free, differently from Arfè et al. (2017a,b) and
455 Mondillo et al. (2018a), who found Mn in some Zn-micas from Cristal. Considering that when
456 studying these assemblages at a finer scale (TEM-HRTEM), the mica particles, as well as other zinc
457 silicates, appeared to be often pervaded by Fe(Mn)-(hydr)oxides (Fig. 13), it is possible that
458 previous EDS-WDS analyses could have been carried out on micas with very fine intergrowths of
459 Fe- and Mn-(hydr)oxides. The simple fact that we found a hendricksitic mica at Mina Grande only
460 and not at Cristal, contrary to Arfè et al. (2017a,b) and Mondillo et al. (2018a), can be also due
461 either a heterogeneous nature of the samples or to an intrinsic limit of the sample selection for TEM
462 analyses, which investigated a restricted area in each specimen.

463 In this study, fraipontite was detected at Mina Grande only, in agreement with Arfè et al. (2017a,b),
464 and has the following empirical formula obtained by AEM study:

465

466 $(Zn_{2.54}Fe_{0.10}Al_{0.50})_{3.14}(Si_{1.24}Al_{0.76})_2O_5(OH)_4$.

467

468 Fraipontite commonly occurs in pore spaces and as well-crystallized individuals with dimension in
469 the range 0.2-3 μm , free of inclusions of other minerals (e.g. Figs. 3 and 4). This rare Zn-clay also

470 crystallized onto the illite surface; indeed, sometimes these two minerals are also in
471 epitaxial/topotaxial relation, with illite acting as a template for the zinc serpentine (Fig. 4c).
472 Contrary to the fraipontite-bearing nonsulfide zinc deposit of Bou Arhous in Morocco (Choulet et
473 al., 2016), at Mina Grande interstratified fraipontite/sauconite minerals were not detected in the
474 fraipontite-rich fractions.

475 Rare trioctahedral and dioctahedral smectites were also found in the Cristal clay fractions.
476 Sauconite has been found in this location in agreement with the findings of Arfè et al. (2018), who
477 described this smectite as mica replacement, as well as occurring in vugs and fracture fillings; its
478 average composition is:

479

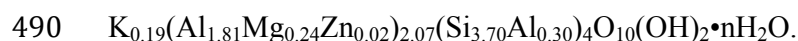


481

482 The average composition of the Accha and Yanque sauconite (Mondillo et al. 2015) is
483 $(\text{Ca}_{0.15}\text{K}_{0.05})_{0.20}(\text{Zn}_{2.10}\text{Mg}_{0.20}\text{Al}_{0.40}\text{Fe}_{0.15}\text{Mn}_{0.02})_{2.87}(\text{Si}_{3.5}\text{Al}_{0.5})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$. Compared with the
484 latter occurrences, K is the only interlayer cation in the Cristal sauconite, and is also richer in Zn
485 and Mn and poorer in Al^{VI} and Mg.

486 Together with sauconite, already reported by Arfè et al. (2017a,b, 2018) and Arfè (2018), the first
487 recorded occurrence of beidellite can be observed in the same location, always with a small Zn
488 amount (0.02 apfu). This clay has the following average formula:

489



491

492 If compared with the composition of the Zn-bearing beidellites found in the Accha and Yanque
493 nonsulfide zinc ore deposits (Mondillo et al. 2015), i.e.
494 $(\text{Ca}_{0.05}\text{K}_{0.15})_{0.20}(\text{Al}_{1.6}\text{Zn}_{0.25}\text{Mg}_{0.1}\text{Fe}_{0.15})_{2.1}(\text{Si}_{3.6}\text{Al}_{0.4})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$, the Cristal beidellite shows

495 interlayer cation only represented by K, lower Zn, higher Mg contents and lacking of Fe. Moreover,
496 also a Zn-bearing montmorillonite (0.14 apfu of Zn) occurs at Cristal, perfectly in line with what
497 was observed in all the Bongará layered silicates.

498 Finally, the kaolinite of Mina Grande has an average formula $(Al_{1.54}Zn_{0.41}Mg_{0.13})_{2.08}Si_{2.05}O_5(OH)$
499 and shows K in trace amount (0.13 apfu), which indicates minor contamination by surrounding illite
500 in the investigated site and explains the anomalous octahedral and tetrahedral sums found.

501

502 **The compositional gap between di- and trioctahedral Zn-phyllsilicates**

503 The first major division in the classification of phyllosilicates is between their dioctahedral and
504 trioctahedral varieties. This is due to the different structural configurations of their respective
505 octahedral layers, with concomitant effects on the corresponding linked tetrahedral layers. In the
506 trioctahedral ones, divalent cations (typically Mg and Fe^{2+}) occupy the three possible positions,
507 accounting for a total charge of $2 \times 3 = 6$. On the other hand, in the dioctahedral ones, trivalent
508 cations (generally Al, but also frequently Fe^{3+}) occupy only two positions, giving $3 \times 2 = 6$ charges.
509 Due to their greater charge, trivalent cations strongly attract anions, producing a smaller octahedron
510 than the divalent ones in the trioctahedral structures, and, certainly smaller than the vacant positions
511 in dioctahedral ones. Therefore, the general structure of the two kinds of layers is significantly
512 different, with three roughly similar octahedrons in the trioctahedral layers, in opposition to two
513 smaller ones and one big irregular position (usually named the *M1* site) in the dioctahedral
514 structures (Moore and Reynolds 1997).

515 As a result, the phyllosilicates always correspond to one of the two types of structures, with a
516 consequential compositional gap between both of them, with a very limited possibility of a solid
517 solution. Therefore, phyllosilicates which have an intermediate composition are rare in nature. The
518 cases of midway chemistry are solved by the existence of nanodomains, as the case of smectites,
519 which appear continuous at the clay particle scale, but are made of associated different lattices or

520 clusters at a finer scale, producing a wide miscibility gap (Grauby et al. 1993; Yamada et al. 1999),
521 or in alternation of the two types of layers, as in sudoite or the limited occurrence of di-trioctahedral
522 interstratified minerals. Therefore, due to the structural constrains, at the unit cell level, a
523 phyllosilicate is either dioctahedral or trioctahedral.

524 In this context, the compositional maps in Fig. 5b and 5c can be considered a graphic representation
525 of the compositional gap between dioctahedral and trioctahedral 2:1 phyllosilicates for the case of
526 Zn varieties. In the phyllosilicates, due to their crystal-chemical characteristics, atomic radio and
527 charge, Zn plays a similar role to Mg and Fe²⁺. Therefore, as a major element it tends to form
528 trioctahedral phyllosilicates, similarly to Mg in phlogopite, saponite, serpentines or tri-chlorites.
529 These would be the equivalent cases of hendricksite, sauconite, fraipontite or baileychlore.
530 However, Mg and Fe (together with other divalent cations, e.g. Mn) can also enter in minor
531 proportion in the typical Al dioctahedral phyllosilicates as muscovite-illite, montmorillonite-
532 beidellite or kaolinite. In a similar way, Zn has been detected in this study in all the aforementioned
533 cases (note that the only exception is baileychlore, which does not occur at Bongará). Zn-bearing
534 varieties of illite (muscovite), beidellite, kaolinite and montmorillonite, have been found together
535 with their trioctahedral counterparts, i.e. K-deficient hendricksite, fraipontite and sauconite, in
536 which Zn is the major or the quite unique octahedral cation.

537 A special consideration needs the case of illite/micas, which are the major constituents of the
538 studied samples. The Cristal and Mina Grande samples mainly consist of Zn-illites. Since they have
539 been formed in a low-temperature environment, these mica-like compositions are genetically
540 conditioned to form as their low-temperature variety, hence to crystallize as illite (Merriman and
541 Peacor 1999; Vázquez et al 2016). Nevertheless, the composition of the fluid from which the micas
542 were grown should have had a Zn content greater than the amount acceptable by the crystal
543 chemistry of dioctahedral illite/mica. Due to the compositional gap between zinc dioctahedral and
544 trioctahedral phyllosilicates, the resultant product was an extremely fine intergrowth of the two

545 varieties: a Zn-illite and its trioctahedral equivalent, i.e. K-deficient hendricksite with Zn as the
546 major octahedral cation. As pointed out by the AEM study, most of the obtained analyses have been
547 unable to resolve the intergrowth, due to its nano-sized nature, under the 20 nm scale (Fig. 5a),
548 resulting in many mixed compositions, i.e. the so-called MDT Zn-illite, as shown in the bivariate
549 plots of Fig. 11 and in the ternary diagrams of Fig. 12. However, the high spatial capabilities of the
550 modern TEMs have allowed obtaining in some limited areas detailed chemical information (as
551 shown in Fig. 5b and 5c), able to reveal the dual nature of the intergrowths (Fig. 5d).

552 The trioctahedral Zn-rich limb of the gap for the low-temperature micas (illite) is difficult to
553 classify due to the lack of previously described equivalents. It shares with hendricksite the major
554 component and the trioctahedral nature. Usually, hendricksite contains also a high quantity of Mn
555 (Robert and Gaspérin 1985; Sharygin 2015), but according to the IMA classification of micas
556 (Rieder et al.1998), this characteristic is not a limiting condition for its classification. Our analyses
557 fulfill the condition of $Zn > 1.5$ apfu, hence the mineral with the studied composition could be
558 considered as hendricksite, but this is not considered one of the K-deficient micas in the IMA
559 classification. Indeed, according to Rieder et al. (1998), the trioctahedral phyllosilicate
560 corresponding to an interlayer-deficient mica is named wonesite, which has a formula
561 $Na_{0.5}\square_{0.5}Mg_{2.5}Al_{0.5}AlSi_3O_{10}(OH)_2$; in the IMA database, the chemical formula of this mineral is
562 reported as $(Na,K,\square)(Mg,Fe,Al)_6(Si,Al)_8O_{20}(OH,F)_4$. The term wonesite is used in the sense of
563 trioctahedral equivalent of illite in the clay literature although, admittedly, following Rieder et al.
564 (1998), it appears as a Na, instead of K, variety. In conclusion, we have indicated the trioctahedral
565 Zn-equivalent of illite as a K-deficient hendricksite. Alternatively, a valid name could be Zn(K)-
566 wonesite, even though a proper term was not predicted in the IMA classification as, to our
567 knowledge, this phase had not been previously described in literature.

568

569 **Origin of the Bongará Zn-phyllosilicates assemblage**

570 Illite is a widespread mica-related clay mineral, uncommon as a surface-derived weathering
571 product, generally formed diagenetically from other clay minerals, such as smectite and kaolinite at
572 temperatures higher than of 70 °C (Einsele 2000). According to Meunier (2005), the range of
573 physical conditions for illite formation are from 20 °C, in surface soil conditions, to below 300 °C,
574 under diagenetic or hydrothermal environments. During diagenesis, with increasing burial, the
575 degree of crystallinity of illite increases, leading to more stable structures. Most studies on
576 illitization report that, as I/S interstratified clays become illitic, the interlayer arrangements change
577 from random (R0) to short-range (R1) ordered, and then to long-range (R3) ordered (e.g. Nieto et
578 al. 1996; Vázquez et al. 2014, and references therein). This occurs at temperatures from 75 to 120
579 °C. The transition from R1- to R3-ordered I/S occurs up to 175 °C, or in other cases at also higher T
580 (Vázquez et al. 2014, and references therein).

581 In the context of nonsulfide Zn(Pb) ores, the zinc-rich clays are frequently detected in supergene
582 deposits, although few studies have provided a clear identification of their nature. In addition, the
583 origin of zinc clays and their place within the ore evolution remain poorly understood (Choulet et
584 al. 2016).

585 The AEM study and the TEM-HRTEM textural evidences of the studied samples suggest that Zn-
586 bearing illite, together with the I3 I/S detected both at Cristal and Mina Grande, could be deposited
587 from a Zn-bearing fluid in a temperature range of 170-200 °C. Considering that Mondillo et al.
588 (2018a), using the mineral geothermometer GGIMFis and the trace element data in sphalerite from
589 the Cristal prospect calculated a possible precipitation temperature (TGGIMFis) of 225±50 °C
590 (slightly higher than in the genesis of typical MVT deposits; Paradis et al., 2007), the studied Zn-
591 illite could have formed during (and/or just after) sulfide precipitation; these TOT sheet silicates
592 hosted Zn²⁺ cations in the octahedral site to various degrees, up to hendricksite-like mineral.
593 Regarding Mina Grande, Arfè et al. (2017b) hypothesized that both a Zn-bearing mica and
594 fraipontite could have formed during the hydrothermal alteration of siltstone or sandstone

595 interbedded within the host limestone, in association with the emplacement of sulfides. The
596 evidences obtained in this study seem to support this genetic model.
597 Regarding fraipontite, its textural arrangement observed by means of TEM-HRTEM suggests that
598 this mineral occurs as a newly formed phase from direct precipitation from Zn(Si,Al)-rich fluids
599 (possibly low temperature hydrothermal), likely at expense of Zn-bearing illite. According to recent
600 studies (i.e. Arfè et al. 2017a; Buatier et al. 2016; Choulet et al. 2016), this TO clay mineral may
601 have formed either during the hydrothermal process that generated the Zn sulfides, or in the early
602 stages of supergene alteration, which took place under acidic conditions associated with the
603 alteration of sulfides. In both cases, when the buffering of the carbonate host rock turned the
604 environment from acidic to alkaline ($\text{pH} > 7$), the fraipontite became unstable and zaccagnaite started
605 to form at its expenses. Arfè et al. (2017a) described by XRD analysis the occurrence of the 3R-
606 polytype zaccagnaite at Mina Grande; they inferred that this particular fraipontite-zaccagnite
607 association could suggest an origin related to weathering processes. However, the present study was
608 not able to definitively confirm or reject this inference about the nature of zaccagnaite and of its
609 origin from a crystal-chemical point of view, because of the tiny size and paucity of their crystals in
610 the samples analyzed.

611

612

IMPLICATIONS

613 This study reveals that the whole of virtually Zn-free phyllosilicates in the Bongará district (Peru)
614 do contain zinc in variable amounts. Among these minerals, Zn-illites are the most widespread in
615 the investigated Zn-rich clayey materials. Considering that deciphering the nature of clay minerals
616 is pivotal for direct implications in the mining industry dealing with base metal recovery/processing
617 of Zn and other metals in nonsulfide deposits (Arfè et al. 2017, and references therein), Zn-bearing
618 illites might not be considered as barren material indeed. In addition, this study indicates that zinc is
619 located within the octahedral sites in each component of the layered silicate forming an intricate

620 mineral assemblage (as also observed in other studies, e.g. Choulet et al. 2016; Balassone et al.
621 2017). Hence it cannot be recovered easily and can only be released by leaching techniques such as
622 solvent extraction, which is relatively efficient for a given clay species like sauconite (Cole and
623 Sole 2002; Boni 2005; Boni et al. 2009a,b; Boni and Mondillo 2015). At Bongará, as in other
624 worldwide occurrences (Choulet et al. 2016), the subordinate occurrence of interstratified clay
625 minerals can have effects in ore liberation, requiring advances for an efficient separation technique
626 and a better selectivity of solvents used.

627 Clay minerals are efficient sinks for base and heavy metals in the geosphere (Churakov and Dähn
628 2012), and the knowledge of the uptake mechanism of these elements on clays, among which there
629 are illite and smectite, can have many important applications in a number of fields of material
630 sciences, including, for instance, protection from industrial pollution and waste, clay based-polymer
631 nanocomposites, heterogeneous catalysts etc. (e.g. Srivastava et al. 2005; Gu and Evans 2007, 2008;
632 Montoya et al. 2018; Zhang et al. 2017). Hence the present work can contribute to an insight into
633 Zn-bearing phyllosilicate systems, by determining the amount/mode of metal incorporation in their
634 lattices and understanding the relationships of naturally occurring complex clay-rich associations,
635 which can act as models for synthetic counterparts.

636 Finally, this research provides an advance in understanding the compositional gap between
637 dioctahedral and trioctahedral layer silicates, with regard to Zn-poor and Zn-rich clays/micas of
638 Bongará, which corresponds to their di- and tri-octahedral varieties respectively. In this case of
639 study, Zn plays in phyllosilicates an equivalent role to Mg and Fe²⁺, with minor presence in the
640 dioctahedral species, together with trioctahedral minerals in which Zn is the major octahedral
641 cation. Among others, this is the case of K-deficient hendricksite - or, if any, Zn(K)-wonesite - the
642 low-temperature variety of Zn trioctahedral mica, whose composition has been firstly described in
643 the current study. It can be predicted that other similar examples will be discovered when
644 appropriate (metal-bearing) systems are examined more closely down to the nanoscale.

645

646

ACKNOWLEDGEMENTS

647 The authors are indebted to M.M. Abad-Ortega and C. de la Prada Sánchez (CIC, Granada) for the
648 skilful support during TEM analyses, and to R. de Gennaro (DiSTAR, Napoli) for his invaluable
649 help during SEM analyses. The authors thank two anonymous Referees, who provided constructive
650 reviews that greatly improved the manuscript, and the Associate Editor Andrew E. Madden for
651 handling manuscript. This work was partly supported by Departmental funds 2017 (University of
652 Napoli Federico II) granted to G. Balassone and by the research projects CGL2016-75679-P from
653 the Spanish Government and the Research Group RNM-179 of the Junta de Andalucía.

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853 LIST OF FIGURES CAPTIONS

854

855 **FIGURE 1.** (a) Geological map of the Bongará district within the Northern Andes morphostructural
856 units B (modified from Arfè et al. 2017b), with location of Mina Grande and Cristal ore fields.
857 (b) Stratigraphic column of the succession in the Bongará area (modified from Brophy 2012).

858

859 **FIGURE 2.** The studied samples from the nonsulfide Mina Grande and Cristal zinc deposits,
860 Bongará (Peru), scale bar is equal to 2 cm.

861

862 **FIGURE 3.** Sample ZB-1 (Mina Grande): (a) textural images of Zn-illite (Zn-Ilt), with fraipontite
863 (Frp). (b) HRTEM image of Zn-Illite in the yellow frame in the image (a), corresponding to a
864 basically disordered polytype, with misorientation among the packets typical of illite (or I3 I/S

865 mixed-layer); the SAED in the inset shows the [100] pattern with reflections (001) at 10 Å of
866 MDT Zn-illite and 9 Å average period in the b* direction. Rows corresponding to (021) and (041)
867 are basically ill-defined diffuse lines, typical of disordered polytypes. (c) HRTEM of another
868 area in yellow circle of (a), with the white fringes likely corresponding to a I3 I/S mixed layer.
869 FFT (inset) shows the misorientation among the layers of the various packets and spacing which
870 correspond to c*, b* and a* of illite and c* of the I3 I/S (4 illite + 1 smectite layers, in crimson).
871 (d) HRTEM image of fraipontite close to Zn-illite, indicated by the sky-blue circle of image (a).
872 (e) Chemical map of Zn-illite (Zn-Ilt), fraipontite and Fe-Ti-oxides (Fe-ox, Ti-ox) of a different
873 zone from the previous ones, with the EDX spectrum referring to Zn-illite of the white frame
874 area. Hereafter the Cu peak visible in the EDX spectra comes from the copper ring used for
875 TEM sample preparation (mineral abbreviations mainly in agreement with Whitney and Evans
876 2010).

877

878 **FIGURE 4.** (a) Textural image of an area in Sample ZB-1 formed by MDT Zn-illite only (MDT Zn-
879 Ilt, see text for acronym explanation); in the inset, SAED [100] + [010] patterns of illite (c* =
880 10Å, a* = 5.2 Å and b* = 9 Å) related to the yellow circle area; (021), (201) and (041) rows are
881 continuous diffuse lines, typical of disordered polytypes. (b) Sample ZB-1, MDT Zn-illite with
882 fraipontite (Frp) and Fe,Ti oxide (Fe-ox, Ti-ox). (c) Sample ZB-2, smooth transition zone of
883 MDT Zn-illite/fraipontite; the inset reports the electron diffraction pattern mainly taken in the
884 left side of the investigated area, displaying rows with the fraipontite (7 Å) and illite (10Å)
885 spacing, in parallel orientation (see text). (d) Sample ZB-1, chemical map of MDT Zn-illite of a
886 different zone from those reported in (a) and (b), with Fe,Ti(Mn) oxide and fraipontite. (e)
887 STEM-EDX spectra 1 and 2 of MDT Zn-illite and fraipontite in image (d).

888

889 **FIGURE 5.** Sample ZB-2 (Mina Grande): (a) textural and (b) chemical map of a zinc illite area (both
890 MDT Zn-Ilt and Zn-Ilt, see text for further explanation), with fraipontite (Frp), kaolinite (Kln),
891 Fe-(hydr)oxides (Fe-ox) and rutile (Ti-ox); the top right inset shows the lattice fringes of the zinc
892 illite area in the white circle. (c) Selected chemical maps (K, Zn and Mg) of the investigated site
893 in (a) and (b). (d) Qualitative EDX spectra of the two areas indicated in image (b). Images a, b
894 and c show the intergrowth between the trioctahedral and dioctahedral micas at the ~20 nm
895 scale.

896

897 **FIGURE 6.** Sample ZB-2: (a) Particles deposited onto a copper grid (CM20 instrument), showing
898 Zn-illite (Zn-Ilt), K-deficient hendricksite (Hnk, see text for explanation), fraipontite (Frp) and
899 Fe(Mn)-oxi-hydroxides (Fe,Mn-ox). (b) Qualitative EDX spectra of K-deficient hendricksite and
900 fraipontite, related to the areas in the red frames of image (a).

901

902 **FIGURE 7.** Sample ZB-2: (a) HAADF and (b) chemical map image of a fraipontite-rich area, with a
903 possible replacement by zaccagnaite (in the dashed areas); see in particular the C peak in the
904 EDX spectrum. (c) Si distribution in image (b).

905

906 **FIGURE 8.** Sample CR07-13 (Cristal): (a) chemical map of Zn-illite (Zn-Ilt) of, with typical
907 differences of composition among the packets. (b) HRTEM and SAED patterns of Zn-bearing
908 illite (black circle area in image a), showing a periodicity of 10 Å. (c) Qualitative EDX spectra
909 of two chemically different areas of Zn-bearing illite in image (a).

910

911 **FIGURE 9.** (a) The Zn-illite-rich area of sample CR07-13, showing differences of orientation among
912 the various packets; SAED in the inset, corresponding to the yellow circle area, shows rows (001)
913 with spacing equal to 10 Å, and the row (021) showing 20 Å periodicity, characteristic of 2M

914 polytype; in addition to [100], other orientations from different packets are also visible in the
915 SAED (b) Another area with prevailing Zn-illite; the left SAED (yellow circle) corresponds to a
916 disordered polytype in [100] orientation, whereas the right one (white circle) includes both rows
917 corresponding to [010] orientation, with a periodicity of 10 Å and to [100] with 20 Å periodicity,
918 characteristic of 2M polytype. (c) HRTEM image of interstratified I/S type, with minor
919 proportion of smectite layers (I3). (d) HRTEM images of Zn-illite, with small disoriented
920 packets.

921

922 **FIGURE 10.** Sample CR13-7 (Cristal): (a) chemical map of Zn-illite (blue areas) interleaved with
923 smectite, corresponding to Zn-bearing beidellite (Bdl, the red areas and related EDX spectrum),
924 and montmorillonite (Mnt); the HRTEM (white circle) demonstrates the occurrence both of
925 smectite and illite. Hemimorphite (Hem) and Fe-(hydr)oxides (Fe-ox) also occur in the
926 investigated area. (b) Chemical map of another zone in the same sample, showing Zn-illite with
927 sauconite (Sau, see also the EDX spectrum) and monazite (Mnz).

928

929 **FIGURE 11.** Bivariate plots of (a) Al_{tot} vs. Si, (b) Zn vs. Al^{VI} and (c) Zn vs. K, expressed in terms of
930 atoms per formula units (apfu), illustrating the compositional variations of clay minerals from
931 Mina Grande and Cristal deposits (point-analyses with bold line refer to compositions
932 approaching Zn-bearing muscovite, see Tables 4 and 5).

933

934 **FIGURE 12.** (a) $4Si-M^{+}-3R^{2+}$ diagram, showing the compositional variations of di- and trioctahedral
935 phyllosilicates of the Bongará samples. The top left inset illustrates selected literature data: ideal
936 muscovite (M), hendricksite (H), sauconite (S), beidellite (B), kaolinite (K) and fraipontite (F)
937 compositions; black line refers to mica, fraipontite and sauconite compositional fields from
938 supergene Zn ores of Bou Arhous, Morocco (Choulet et al. 2016); red line fields are related to

939 sauconite, beidellite and muscovite from Skorpion, Namibia (Balassone et al. 2017); blue line
940 fields are referred to beidellite (left) and sauconite (center) compositions from Peru (Mondillo et
941 al. 2016). (b) Schematic compositional fields of Zn-bearing phyllosilicates of Mina Grande and
942 Cristal in the K-Zn-Al^{VI} system. The top left inset shows compositions of ideal compositions of
943 muscovite (M), hendricksite (H) and fraipontite (F) plotted in the same diagram (from IMA
944 database and Mondillo et al. 2018, and references therein) (point-analyses with bold line as in
945 Fig. 11).

946

947 **FIGURE 13.** Chemical mappings of the typical infiltration of Fe-Mn (hydr)oxides in zinc silicates at
948 very fine scale: (a) Fe(Mn)-ox (mainly Mn-bearing goethite) with Zn-illite (Zn-IlI); (b)
949 chalcophanite with hemimorphite (sample CR13-7).

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953

954 **Table 1.** Theoretical formulae of Zn-bearing phyllosilicates and other selected minerals cited in the
955 text (IMA database, <http://rruff.info/ima/>).

956

957 **Table 2.** Selected structural formulae of phyllosilicates from sample ZB-1, in atoms per formula
958 units (apfu), calculated on the basis of 11 oxygens for MDT Zn-illite and K-deficient
959 hendricksite, 6 octahedral+tetrahedral cations for Zn-illite (as in Nieto et al. 2010) and 7 oxygens
960 for fraipontite.

961

962 **Table 3.** Selected structural formulae of phyllosilicates from sample ZB-2, in atoms per formula
963 units (apfu), calculated on the basis of 11 oxygens for MDT Zn-illite and K-deficient

964 hendricksite, 6 octahedral+tetrahedral cations for Zn-illite (as in Nieto et al. 2010) and 7 oxygens
965 for fraipontite and kaolinite.

966

967 **Table 4.** Selected structural formulae of phyllosilicates from sample CR07-13, in atoms per formula
968 units (apfu), calculated on the basis of 11 oxygens for Zn-illite MDT and 6
969 octahedral+tetrahedral cations for Zn-illite and muscovite (as in Nieto et al. 2010).

970

971 **Table 5.** Selected structural formulae of phyllosilicates from sample CR13-7, in atoms per formula
972 units (apfu), calculated on the basis of 11 oxygens for Zn-bearing illite MDT, sauconite,
973 beidellite and montmorillonite and 6 octahedral+tetrahedral cations for Zn-bearing illite and
974 muscovite (as in Nieto et al. 2010).

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